

## XAFS analysis on the interaction between RuO<sub>2</sub>/CeO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>

Saburo HOSOKAWA, Toshiya NISHIGUCHI, Hiroyoshi KANAI, Seiichiro IMAMURA\*  
Department of Chemistry, Kyoto Institute of Technology, Kyoto 606-8585, Japan

### INTRODUCTION

CeO<sub>2</sub> is an evitable component in the automobile catalyst; it keeps high surface area, prevents sintering of noble metals, and thus, stabilizes their dispersed state. We found that the amount of C<sub>3</sub>H<sub>6</sub> adsorbed on RuO<sub>2</sub>/CeO<sub>2</sub> was peculiarly larger than those on Pt-, Pd-, and Rh/CeO<sub>2</sub>. The interaction between RuO<sub>2</sub>/CeO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> was investigated by XAFS analysis.

### EXPERIMENTAL

Ce(OH)<sub>3</sub> was precipitated from aqueous Ce(NO<sub>3</sub>)<sub>3</sub> with NaOH at pH of about 11. The precipitate while it was wet, was dispersed in deionized water. A known amount of RuCl<sub>3</sub> was added followed by introducing HCHO under stirring at 90 °C for 1 h. Then 3 N-NaOH was added to the mixture until the pH of the solution was about 11. The solid portion was filtered and washed with deionized water followed by drying at 80 °C overnight and calcination at 500 °C for 3 h in air. XAFS measurements were carried out using a reaction cell. RuO<sub>2</sub>/CeO<sub>2</sub> was pretreated with O<sub>2</sub> at 200 °C for 1 h, was cooled to room temperature and the spectra were recorded. Then, the cell was evacuated to remove O<sub>2</sub>, C<sub>3</sub>H<sub>6</sub> was introduced on the catalyst for 15 min at room temperature and the spectra were also recorded.

### RESULTS AND DISCUSSION

The Ru K-edge XANES spectra are shown in Fig. 1. The pre-edge peak was not detected in RuO<sub>2</sub> but it was observed at 22115 eV for the RuO<sub>2</sub>/CeO<sub>2</sub> pretreated with O<sub>2</sub>. The pre-edge peak is caused by the transition from 1d to 4d level of metal ions. Although this transition is formally forbidden, asymmetric configurations of metal ions allow it. As RuO<sub>2</sub> has a good symmetry with six coordinated structure, the pre-edge peak is not detected. However, as the pre-edge peak was detected in the O<sub>2</sub>-treated RuO<sub>2</sub>/CeO<sub>2</sub>, we deduced that the state of the Ru species was more asymmetric than RuO<sub>2</sub> and was in a five-coordinated structure. When C<sub>3</sub>H<sub>6</sub> was introduced to the RuO<sub>2</sub>/CeO<sub>2</sub>, the pre-edge peak was disappeared.

Therefore, the Ru species with the five coordinated structure on CeO<sub>2</sub> reacted with C<sub>3</sub>H<sub>6</sub> and Ru seemed to change to six coordinated structure.

The FT peak intensity of RuO<sub>2</sub>/CeO<sub>2</sub> pretreated with O<sub>2</sub> was lower than that of RuO<sub>2</sub> and the peak pattern of RuO<sub>2</sub>/CeO<sub>2</sub> was different from RuO<sub>2</sub> in the region of 3.0 Å (Fig. 2). Therefore, we considered that two Ru species were dispersed on CeO<sub>2</sub>: the most of Ru species formed RuO<sub>2</sub> and a part of Ru species highly dispersed on CeO<sub>2</sub> formed Ru-O-Ce bonds. The FT's of RuO<sub>2</sub>/CeO<sub>2</sub> after introduction of C<sub>3</sub>H<sub>6</sub> is similar to RuO<sub>2</sub>. Therefore, the oxygen atoms of Ru-O-Ce bonds were reacted with C<sub>3</sub>H<sub>6</sub> but Ru-O-Ru in RuO<sub>2</sub> was not reacted and remained. From this results, we consider that RuO<sub>2</sub>/CeO<sub>2</sub> pretreated with O<sub>2</sub> have highly dispersed Ru species on CeO<sub>2</sub>, which forms Ru-O-Ce. This is in the five coordinated structure and reacts with C<sub>3</sub>H<sub>6</sub>.

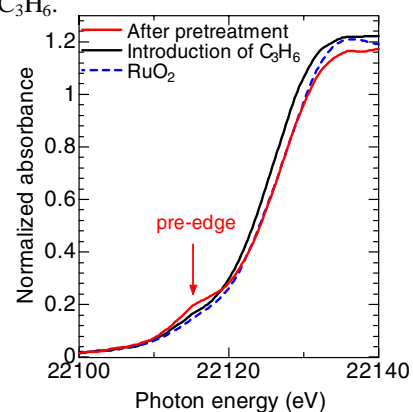


Fig. 1 Normalized XANES spectra of Ru (K-edge).

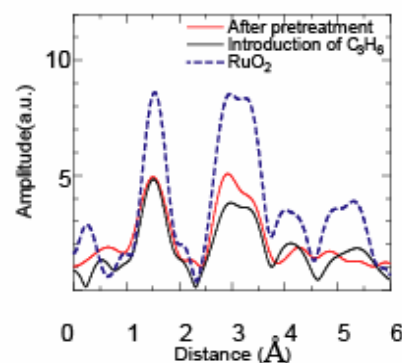


Fig. 2 EXAFS-FT of Ru supported on CeO<sub>2</sub>.

imamura@kit.ac.jp